UV RAMAN DETECTION OF CHEMICAL AGENTS

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ABSTRACT

Optical detection techniques are attractive because they are non-intrusive and, in the case of vibrational spectroscopy, highly selective. Like infrared absorption and UV fluorescence, Raman spectroscopy has advantages and limitations as a non-contact detection and identification technique. One area where it appears to be well suited is for the detection of liquid and solid contamination on surfaces. In a effort to develop a UV Raman based surface contamination detector, we have measured the UV Raman signatures and cross sections of chemical agents, simulants, and possible interferents as well as a number of toxic industrial chemicals and materials. In addition to the target chemicals, we have also characterized the Raman return from surfaces such as concrete, asphalt, and vegetation.

1. BACKGROUND

The Raman technique entails irradiation of the sample with a monochromatic source, typically a laser, and spectroscopically analyzing the scattered light. A spectrum corresponding to characteristic vibrational frequencies of the material is obtained to the red of the source frequency (the Stokes spectrum) and a similar spectrum is repeated to the blue of the exciting source (the anti-Stokes spectrum), the latter being much weaker at room temperature. The Raman lines are shifted from the excitation wavelength by amounts equal to the vibrational frequencies of the molecule. In normal Raman measurements the spectrum is quite weak, typically 1 part in 10^4 to 10^6 of the excitation intensity. However, with modern spectrographs, filters, lasers, and detectors, high signal-to-noise Raman spectra consisting of sharp, well-defined lines can be obtained from a variety of materials. The intensity and quality of the Raman spectrum depend on the Raman scattering cross section, the degree of absorption and interfering fluorescence, and the thermal and photochemical stability of the sample under excitation.

The Raman cross section itself is dependent on the excitation wavelength to the inverse fourth power resulting in higher Raman intensity with shorter wavelength laser excitation. This is one of the main advantages to using UV laser excitation for detecting agents on surfaces. Another advantage is that shifting to excitation wavelengths below about 250 nm actually shifts the Raman spectrum away from the tryptophan fluorescence band found in biological material. At higher wavelengths, the tryptophan fluorescence can obscure the weaker Raman signals. The final advantage to UV excitation is that Raman spectrum is manifest in the solar blind region of the spectrum.

2. RESULTS:

A prototype Raman surface detector has been built and tested in the laboratory with both chemical agents and simulants. The detector has been named LISA (Laser Interrogation of Surface Agents) by the developer, ITT Industries. A necessary component of the technology development is the measurement of Raman signatures and cross sections of target chemicals and surfaces. The results of this science base work will be the focus of this presentation.

The hallmark of Raman spectroscopy is its ability to differentiate structurally similar chemicals. This is illustrated in figure 1 with the spectra of the chemical agents GB and GD. Although they differ only in the number and conformation of the methyl groups attached to the oxygen (isopropyl methyl for the former and pinacolyl methyl for the latter) the spectra are easily differentiated.

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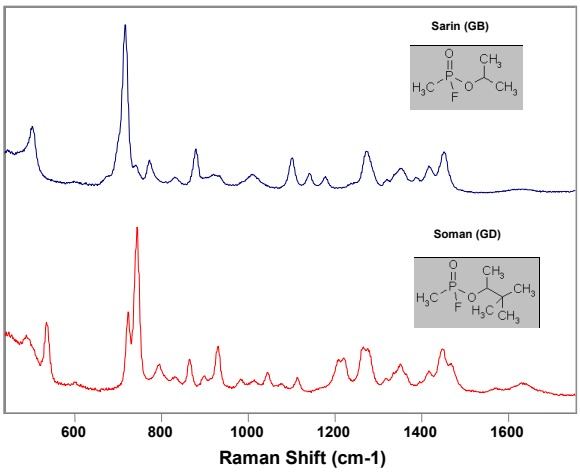

Figure 1: UV Raman Spectra of GB and GD.

The Raman intensities as represented by the differential Raman scattering cross sections have also been measured for the chemicals of interest (Table 1). These results are used with the UV absorption data to calculate a relative sensitivity for the chemical agents and simulant.

Table 1: Raman Cross Sections and Relative Signals.

Agent / Simulant	Raman Line (cm^{-1})	Cross Section (cm^2/sr/ molecule)	α_0 (cm^{-1})	α_r (cm^{-1})	Relative Signal (calc.)	Relative Signal (meas.)	Calc. / Meas.
DEM	1747	2.1E-28	43	25	1.0	1.0	***1.00***
MeS	1680	1.3E-25	15640	15640	1.6	1.8	***0.91***
TEPO	729	2.4E-28	1	1	27	28	***0.96***
DMMP	701+710	5.6E-28	15	11	10	8	***1.21***
DCE	748	4.6E-28	2	2	59	173	***0.34***
HD	1296	2.23E-28	441	359	0.1	0.1	***1.01***
GB	718	1.2E-28	6	6	3.9	3.7	***1.07***
GD	745	1.8E-28	14	14	1.8	1.5	***1.23***
GA	2250	4.1E-28	34	14	2.7	2.9	***0.95***

Equation 1

$$\text{Raman Signal} \propto \frac{d\sigma}{d\Omega} \times \rho \times \int_0^D 10^{-(\alpha_0+\alpha_R)r}\, dr$$

$\frac{d\sigma}{d\Omega} \equiv$ Raman Cross Section

$\alpha_0 \equiv$ absorptivity at 248nm

$\alpha_0 \equiv$ absorptivity at the Raman line

$\rho \equiv$ molecular density

$D \equiv$ sample thickness

In Table 1, the column marked relative signal is the Raman Signal calculated using equation 1 for the agent or simulant divided by the calculated signal for DEM. The Calc./Meas. column is the ratio of the calculated relative signal from the previous column divided by the relative signal actually measured by the LISA system. The agreement between calculated and measured are quite good, and argue for the overall validity of the model used. This analysis allows for the direct comparison of sensitivities observed for simulants to what can be expected for the actual agents.